Iron-based layered superconductor $LaO_{1-x}F_xFeAs$: an antiferromagnetic semimetal

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We have studied the newly found superconductor compound $LaO_{1-x}F_xFeAs$ through the first-principles density functional theory calculations. We find that the parent compound LaOFeAs is a quasi-2-dimensional antiferromgnetic semimetal with most carriers being electrons and with a magnetic moment of $2.3\mu_B$ located around each Fe atom on the Fe-Fe square lattice. Furthermore this is a commensurate antiferromagnetic spin density wave due to the Fermi surface nesting, which is robust against the F-doping. The observed superconduction happens on the Fe-Fe antiferromagnetic layer, suggesting a new superconductivity mechanism, mediated by the spin fluctuations. An abrupt change on the Hall measurement is further predicted for the parent compound LaOFeAs.

Just recently an iron-based layered compound LaOFeAs was reported to show superconductivity after doping F atoms to replace O atoms at a concentration of 3-13 atom%, with the highest critical temperature of about 26K[1]. In comparison with those high T_c superconductors which superconduction happens on CuO_2 layers[2], the compound LaOFeAs possesses conduction at iron-based FeAs layers and further goes superconducting after doping F atoms. This strongly suggests that there be a new superconductivity mechanism underlying because unlike the case of superconduction at CuO_2 layers it is the transition metal atoms, especially here the Fe atoms, that directly play a role in conduction and superconduction, in which there would be many interactions and degrees involved, like electronic and magnetic.

Clearly, the understanding of electronic and magnetic structures of the parent compound LaOFeAs and its F-doped derivatives is the key basis to understanding the new possible superconductivity mechanism underlying. There have now been a number of theoretical works with target of understanding electronic structure of the compound LaOFeAs [3, 4, 5]. All of these works find that the compound LaOFeAs is a nonmagnetic metal with a low density of carriers and its normal phase is located at the borderline of magnetic phases. The work [5] further suggests that the correlated effect would be considered.

It is well-known that at low temperatures in the order of $3d$ transition metals in their element form, Cr and Mn usually take antiferrogametic state while Co and Ni are ferromagnetic, the in-between Fe displays a variety of magnetic phases, for example, bcc-Fe is a strong ferromagnet, but fcc-Fe may be nonmagnetic, ferromagnetic, antiferromagnetic, or spin density wave, dependent upon the local environment and the lattice constant [6]. Accordingly, we expect that the Fe atoms would show novelty in LaOFeAs compound. Indeed our first-principles calculations show very interesting finding that the compound LaOFeAs is an antiferromagnetic (AFM) semimetal rather than nonmagnetic (NM) metal due to the Fermi surface nesting.

We performed the first-principles density functional theory electronic structure calculations by using the plane wave basis method[7]. In the calculations, we adopted the local (spin) density approximation (L(S)DA) and the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)[8] for the exchange-correlation potentials. And the ultrasoft pseudopotentials [9] were used to model the electron-ion interactions. After the full convergence test, the kinetic energy cut-off and the charge density cut-off of the plane wave basis were chosen to be 800eV and 4800eV, respectively. The Gaussian broadening technique was used and a mesh of $36 \times 36 \times 18$ k-points were sampled for the Brillouin-zone integration. For all relaxed structures, the convergence sets by the forces being smaller than 0.01eV/Å.

The parent compound LaOFeAs crystallizes in a tetragonal layered structure, being a member of quaternary oxypnictide family LaOMPn (M=Cr, Mn, Fe, Co, and Ni, Pn=P and As). Its unit cell, also adopted as the calculation cell, consists of two formula subunits with eight atoms limited to the symmetry of $P4/nmm$ space group, in which FeAs layers and LaO layers are arranged alternating along the c axis. In the calculations, the experimental lattice parameters a=4.03552Å, c=8.7393Å were adopted while the two internal coordinates of La and As atoms within the cell were determined by the energy minimization. We emphasize the Fe atoms form a 2-dimensional square lattice with a separation of 2.85Å. To the end, we checked the lattice parameters by the energy minimization, and find less than 1% change so that there are no meaningful changes on the results.

We first studied the NM state of the compound LaOFeAs, which means spin degrees were not included in the calculation. Such a study provides a reference for studying magnetization states, by analyzing which we can better understand the mechanism underlying the magnetization if existing. It turns out that our calculated results on the NM state are similar to those in Ref.
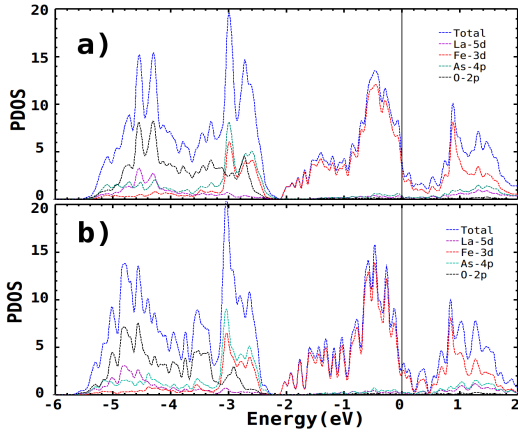
FIG. 1: (Color online) Calculated atomic orbital-resolved partial density of states of $LaO_{1-x}F_xFeAs$ in nonmagnetic state. (a) parent compound LaOFeAs; (b) $LaO_{0.95}F_{0.05}FeAs$ (5% F-doping). The Fermi energy sets to zero.
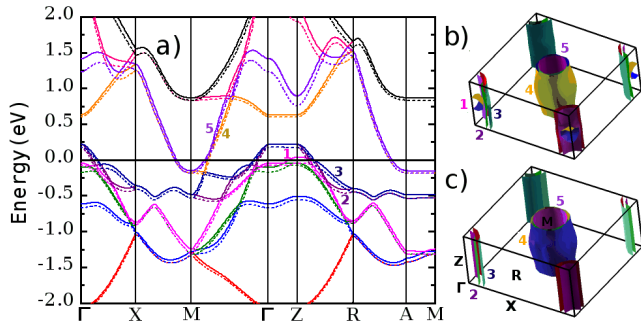

FIG. 2: (Color online) Calculated nonmagnetic electronic structures of $LaO_{1-x}F_xFeAs$. (a) energy band structures: the solid lines for the undoping while the dotted lines for the 5% F-doping (the Fermi energy sets to zero); (b) undoping: Fermi surface; (c) 5% F-doping: Fermi surface.

[3, 4, 5]. From Fig. 1(a), we see that the density of states (DOS) may be divided into two parts, i.e. the lower part (2eV below the Fermi energy) consists of those bands formed through the bonding between O and La atomic orbitals and Fe and As atomic orbitals, and the upper part consists basically of the Fe-3d orbital bands ranging from -2eV to 2eV centered at the Fermi energy. Further analyzing of the calculation shows that the crystal field effect upon the Fe-3d orbitals is much weaker than in transition metal oxides, which is understandable because the electronegativity of As is much smaller than that of O. Thus all Fe-3d electrons are expected to play a dominant role in conduction and related superconductivity if LaOFeAs is nonmagnetic.

Fig. 2(b) shows that the Fermi surface is made up of five sheets, derived from the five bands crossing the Fermi energy marked by numbers in Fig. 2(a). Among these five sheets, the two sheets due to two electron bands marked by 4 and 5 are forming two cylinder-like
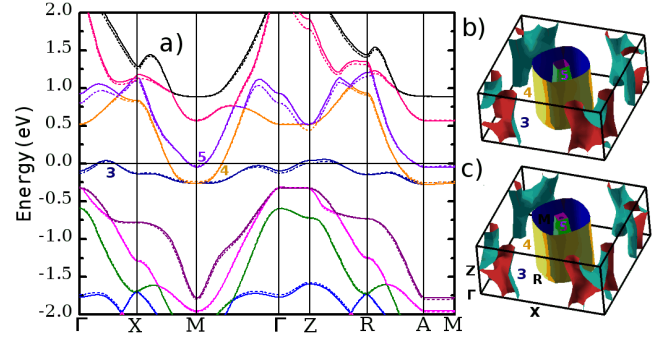

FIG. 3: (Color online) Calculated antiferromagnetic electronic structures of $LaO_{1-x}F_xFeAs$. (a) energy band structures: the solid lines for to the undoping while the dotted lines for 5% F-doping (the Fermi energy sets to zero); (b) undoping: Fermi surface; (c) 5% F-doping: Fermi surface. Note that here only the spin-up part is shown.

shapes centered around M-A; and the other three due to three hole bands marked by 1, 2 and 3 are forming two cylinder-like shapes centered around Γ-Z and one pocket around Z, respectively. As we see, because of nearly no the band dispersion along (001), the conduction is strongly anisotropic, only happening on the FeAs layers. The volumes enclosed by these Fermi sheets give 0.28 electrons/cell and equally 0.28 holes/cell, namely $1.97 \times 10^{21}/cm^3$. The compound LaOFeAs in the NM state is thus a semimetal with a low carrier density, between normal metals and semiconductors.

The F-doping effect upon the electronic structures of $LaO_{1-x}F_xFeAs$ were studied at $x = 3\%$, 5%, 8%, 10%, and 15% by using virtual crystal calculations. Fig. 2(a) shows that the 5% F-doping just relatively moves the Fermi level slightly up, i.e. increasing the number of electrons while reducing the number of holes in the unit cell. This is also clearly shown by changes of the Fermi surface shown in Fig. 2(c), in which the hole pocket disappears and the two hole cylinders shrink while the two electron cylinders expand obviously. Such a change is found up to the 15% F-doping. Thus the F-doping effect can be basically considered as doping electrons. On the other hand, Fig. 1 (b) shows that the density of states at the Fermi energy heavily decreases with the F-doping, which suggests that the doping in the NM state may not favor the superconductivity even though the total electron carrier density increases. The doping also introduces more wiggles in the DOS (Fig. 1 (b)).

We next included spin degrees to study magnetization states of the compound LaOFeAs. Here we define the spin density polarization as the ratio of the difference to the sum, between the charge densities with spin up and spin down. We first broke the spin up-down symmetry by assigning ferromagnetic moments to the Fe atoms. It turns out no matter how large to assign the initial moments, the system always evolves into a NM state without
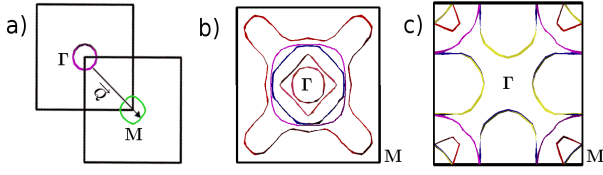
FIG. 4: (Color online) Calculated nonmagnetic Fermi surface cross sections through Γ and M in (001) plane. (a) LaOFeAs: the nesting vector is denoted by $\vec{Q} = (\frac{\pi}{a}, \frac{\pi}{a}, 0)$, between Γ and M, a being the lattice constant; (b)LaOMnAs; (c) LaOCoAs.
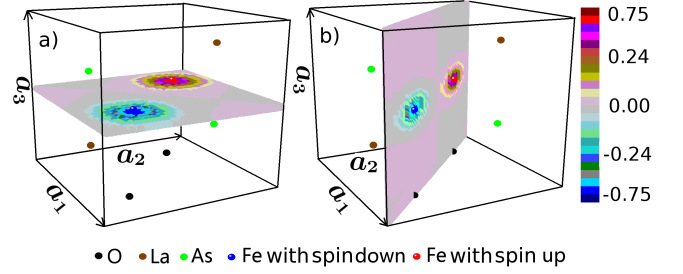

FIG. 5: (Color online) Calculated antiferromagnetic spin-polarized charge density distribution in the LaOFeAs unit cell: (a) in the Fe-Fe square lattice plane; (b) perpendicular to the Fe-Fe square lattice plane. Here the red part denotes spin up and the blue part denotes spin down.

any local moment remaining, namely back to the initial NM state. LaOFeAs will thus not display ferromagnetic. We then assigned AFM moments to the two Fe atoms in the unit cell to break the spin up-down symmetry. We find that when the initial AFM assignment is with the spin density polarization set less than 6%, the system still evolves back into the NM state. However, when the spin density polarization set larger than 6%, the system evolves into a stable AFM state with the energy lowered by 0.16 eV/cell. The internal coordinates of As and La in the unit cell can be further relaxed, which lowers the energy by extra 0.06 eV/cell. Eventually this AFM state is more stable in energy by 0.22 eV/cell than the NM state. Finally about a $2.38\mu_B$ magnetic moment is formed around each Fe atom. We have thus shown that there exist two stable states, namely the NM state and the AFM state, in electronic degree configurations for the compound LaOFeAs. Between the two states, the AFM state is more favorable in energy to be the ground state and the NM state is then to be a metastable state. We also did the independent calculation by using the full potential linearized augmented plane wave (FLAPW) method with the code WIEN2K package[10], which also indicates the LaOFeAs ground state is antiferromagnetic.

In comparison with the NM state (Fig. 2), there are now just three bands crossing the Fermi energy (Fig. 3), the previous two bands 1 and 2 in Fig. 2(a) are now pushed down much, making the hole pocket and one hole cylinder disappear in the AFM state. Meanwhile, the bands 4 and 5 in Fig. 2(a) nearly emerging around M and A are now splitting, in which the band 4 is going down while the band 5 is going up in the AFM state. These changes on the energy band structure overall make the AFM state more favorable in energy. This can apparently be attributed to the exchange energy lowering. However, when we compare the Fermi surfaces between the NM (Fig. 2(b)) and the AFM (Fig. 3(b)) states, we find that there exists the Fermi surface nesting in the NM Fermi surface that may induce the AFM Fermi surface, as shown in Fig. 4(a). The nesting vector is $\vec{Q} = (\frac{\pi}{a}, \frac{\pi}{a}, 0)$ between the hole sheets and the electron sheets. Fig. 5 plots the calculated AFM spin polarized charge density distribution in the LaOFeAs unit cell, which indicates that the AFM state is a quasi-2-dimensional AFM spin

density wave, oscillating as $\vec{M}\cos(\vec{Q}\cdot\vec{R})$ on the Fe-Fe square lattice with a wave vector equal to the nesting vector $\vec{Q}$ ($\vec{R}$ being the lattice site vector). We thus conclude that the underlying physics to stabilize the AFM state is the Fermi surface nesting. It turns out that the AFM electronic structure is quite different from the NM one, especially around the Fermi energy.

From the calculated AFM density of states shown in Fig. 7, we see a gap opens around -0.5eV in contrast to the NM state in Fig. 1(a) because of the Fermi surface nesting. This is also reflected between the band structures of the NM and AFM states (Fig. 2(a) and Fig. 3(a)). Corresponding to this opening, the more states are pushed down to around -2.0eV. Meanwhile, the density of states at the Fermi energy becomes larger (Fig. 7(a)), being nearly double (spin up plus down) of that in the NM case (Fig. 1(a)). The projected density of states in Fig. 6 further shows that there is basically no contribution from the Fe-$3d_{x^2-y^2}$ orbitals between -0.6eV and 0.6eV centered at the Fermi energy while the Fe-$3d_{z^2}$ with $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$ are dominant in this range. Physically this is because the Fe-$3d_{x^2-y^2}$ orbitals have formed so strong bond along the nearest Fe-Fe direction that the derived band is very below the Fermi energy. Further inspection of the calculations shows that the hole portion in Fig. 3(b) consists mostly of the Fe-$3d_{z^2}$ orbitals with a very small portion of As-$4p_z$ orbitals while the two electron cylinders consist of the Fe $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$ orbitals. Moreover, in the AFM state, the volumes enclosed by the Fermi surface sheets in Fig. 3(b) yield 0.26 electrons/cell (1.83×10^{21}/cm^3) and 0.12 holes/cell (0.84×10^{21}/cm^3), respectively. Thus the parent compound LaOFeAs is an AFM semimetal with most carriers being electrons. Note that in the NM state, the carrier densities of electrons and holes are equal. So we predict that there will be an abrupt change in the Hall measurement for the compound LaOFeAs from high temperatures to low temperatures, corresponding to the transition from the NM phase to the AFM phase.

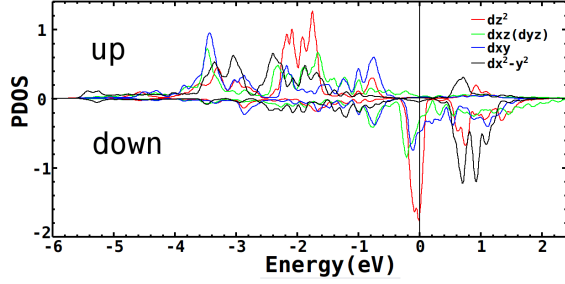We also undertook further calculations to check how

FIG. 6: (Color online) Calculated antiferromagnetic density of states projected into the Fe-3d atomic orbitals around one of the two Fe atoms in the unit cell. Note that the spin-up and the spin-down is reversed around the other Fe atom.
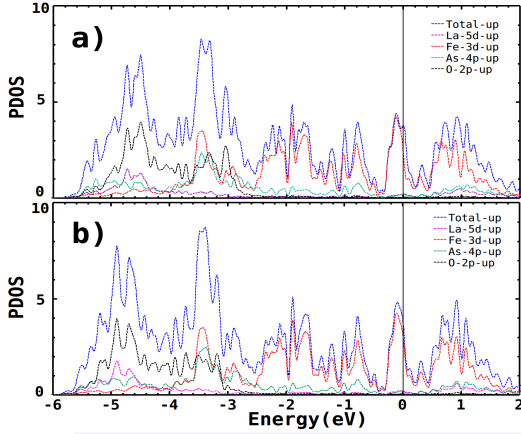

FIG. 7: (Color online) Calculated atomic orbital-resolved partial density of states of the compound $LaO_{1-x}F_xFeAs$ in antiferromagnetic state. The Fermi energy sets to zero. (a) parent compound LaOFeAs; (b) $LaO_{0.95}F_{0.05}FeAs$ (5% F-doping). Note that here only the spin-up part is shown.

stable this AFM state is under the F-doping. Similar to the NM case (Fig. 2(a)), Fig. 3(a) shows the 5% F-doping is also just rigidly to move the Fermi level slightly up, increasing the number of electrons while decreasing the number of holes in the unit cell. The volume enclosed by hole Fermi surface sheet number 3 shrinks obviously in Fig. 3(c). We find such a change on the electronic structure is taken until the 15% F-doping with negligible effect on the AFM spin density wave. So the AFM state is stable against the F-doping. The F-doping effect on the AFM phase is also basically to dope electrons. Unlike in the NM state, the density of states at the Fermi energy now decreases not much with doping (Fig. 7(b)).

We notice that the superconductivity takes place in experiment when the F-doping concentration is between 3% and 13% [1], in which concentration range the compound $LaO_{1-x}F_xFeAs$ in normal phase will hold the AFM spin density wave according to our calculations. Further the itinerant Fe-3d electrons are also dominant around the Fermi surfaces, so the superconductivity goes working on the AFM layers with the electron pairing, we suggesting,

mediated by the spin fluctuations.

We also carried out the calculations in order to search for the trend in line of M=Cr, Mn, Fe, Co, and Ni in LaOMAs and LaOMP. The calculated results are similar to those reported in Ref. [4] except for LaOFeAs that has been reported and analyzed in this Letter. The scrutiny of the Fermi surface structures further evinces that there is no more Fermi surface nesting, at least no commensurate nesting existing, as shown in Fig. 4 (b) and (c). The Fermi surface nesting only happens on LaOFeAs, being underlying mechanism of its AFM, which makes LaOFeAs distinct from the others in the line.

In conclusion, our studies indicate that the parent compound LaOFeAs is a quasi-2-dimensional antiferromagnetic semimetal, in which the antiferromagnetic spin density wave forms on the Fe-Fe square lattice due to the Fermi surface nesting. This antiferromagnetic state is robust against the F-doping. This provides a new platform on which the superconductivity takes place, strongly implying a new superconductivity mechanism underlying. An abrupt change is predicted for the Hall measurement due to different carriers between the nonmagnetic and antiferromagnetic phases.

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